



APPENDIX B

Electrochemical Etching of Thick Copper Patterns on Circuit Substrate

Etching of copper circuit patterns on substrates, such as printed circuit boards (PCB), is normally done by chemical etching in a ferric chloride solution. However, the isotropic nature of the etching process presents problems when etching thick copper layers (5 - 10 mil). Because of the prolonged immersion, the sidewalls also undergo substantial sideways etching resulting in a grossly widened and irregular pattern. An electrochemical method of etching thick copper patterns was tested with promising results. The method is like electroplating in reverse with adjustable etching rate, easily scalable and relatively low cost. The etching solution is reusable and thus minimizes the production of waste solution. Results of our comparative study of 8-mil thick Cu patterns etched electrochemically and in FeCl_3 solution show that the former gives better line definition than the traditional method. The anisotropic and self-terminating nature of the electrochemical technique not only minimizes undercutting but also prevents overetching. The method may be extended to other types of metal that can be electroplated.

I. Introduction

Circuit boards are usually fabricated from glass fiber reinforced epoxy printed circuit boards (FR-4)[1] with copper layers of 1 to 2 mil (25 to 50 μm) thick. The desired circuit pattern is reproduced on the board by applying a thin coating of light-sensitive material (photoresist) that can be patterned and developed followed by chemical etching in a concentrated ferric chloride solution. Boards produced in this manner are usually adequate for most low-power applications. However, for high-power applications, large currents and high voltages demanded by the applications require circuit boards that can carry high current loads and efficiently dissipate large amounts of heat. For example, direct-bond copper (DBC)-aluminum nitride substrate is a common material used in power modules.[2] Aluminum nitride has a significantly higher thermal conductivity than the glass fiber-reinforced polymer boards.[3] The DBC metallization provides heat spreading and high current carrying capability at the same time. The copper layer is typically

10 mil (250 μm) to 20 mil (500 μm) and therefore is capable of handling larger currents. However, the thicker copper also means a longer etching time for producing the pattern. Because chemical etching with ferric chloride is isotropic or nondiscriminate, the degree of overetching also increases resulting in gaps that may be wider than what is tolerable. The design of closer lines and narrower gaps leads to the lengthening of the etching time. Also, the reproducibility and control of the transfer (etching) of patterns in the 100-200 μm range on 10-mil thick copper substrate can be difficult with ferric chloride etching. Another disadvantage is that the bath chemistry is specifically formulated for copper and its alloys, Kovar and steel.[4]

An alternative procedure for etching the copper layer is by electrochemical method. This is simply the reverse of electroplating, a metal-deposition process that is well-known and widely used for various applications.[5] The substrate being etched acts as the anode in the electrochemical cell. The cathode is also made of copper or any copper-coated board. Since the quality of the copper plated on the cathode is not a primary concern, the choice of plating bath composition will be dictated by the pattern quality required for the anode and the potential reaction between the mask, e.g., photoresist, and the plating bath. For this work, an alkaline solution was not desirable because it attacks the photoresist, a problem that can easily be eliminated by switching to another masking material. The operating current density can also be higher than what is recommended for plating. The choice of the current density would therefore be a balance between acceptable etching times and the limitations of the underlying process itself. One advantage of this process is that by running the cell under proper conditions, the bath can be reused many times with minimal reconditioning along the way. Another advantage is its potential applicability to many other types of metals that can be electroplated.

II. Theoretical Considerations

There are basically two processes going on that we have to consider in an electrochemical cell. At the anode, a dissolution reaction takes place. The half-cell reaction can be represented by a simple equation as follows



where M is the reduced state of the metal, M^{n+} is the metal ion, n is the oxidation state of the metal ion, and e^- is the electron released by the reaction. The potential, E , for the anodic reaction is given by the Nernst equation [5]

$$E = E^{\circ} - \frac{RT}{nF} \ln Q \quad (2)$$

where E° is the standard potential, R is the gas constant, T is the temperature, F is the Faraday constant (96500 Coul/mol) and Q is the equilibrium constant for the cell reaction. For the reaction in Eq. (1), Q is expressed in terms of the activities of the products and reactants

$$Q = \frac{a_{M^{n+}}}{a_M} \quad (3)$$

The cathodic reaction on the other hand is just the reverse of the anodic reaction, which in this case would be the reduction and deposition of the metal on the cathode. This is given by the following



The corresponding half-cell potential for the reduction reaction also given by Eq. (2) is simply the negative of the potential for the dissolution reaction since the electrolyte is the same for either half-cell. The equilibrium constant will be the inverse of Q for the anodic reaction. Therefore, the reaction potential for the combined reduction-oxidation process is zero. However, in practice, a voltage is applied across the two electrodes to overcome resistances in the cell circuitry and to get a reasonable reaction rate in the desired direction.

The discussion above merely accounts for the thermodynamic aspects of the process. The kinetics of the process is more important because it determines the practicality of the method as compared to chemical etching. Since the process is conducted under non-equilibrium conditions, it is necessary to deal with the electrode kinetics of the reactions involved.

Under equilibrium conditions, there is no distinction between the cathode and the anode for two identical half-cells, which is what we are dealing with, so an analysis of one electrode will apply to the other. At the electrode, there are two terms associated with the current density: (a) the anodic current density, i_+ , corresponding to dissolution and (b) the cathodic current density, i_- , corresponding to reduction. The net current density at the electrodes can then expressed as

$$\text{Cathode:} \quad i_{net} = i_- + i_+ \quad (5a)$$

Anode:
$$i_{net} = i_+ + i_- \quad (5b)$$

The magnitude and direction of the net current density will depend on the potential of the electrode. There exists a potential at which the net current is zero and this potential is referred to by several names as the equilibrium potential, reversible potential or thermodynamic potential, E_{rev} . At this potential, the magnitudes of the anodic and cathodic current densities are the same and equal to what is referred to as the exchange current density, i_o . When the potential moves away from the equilibrium voltage, that is an overvoltage η is applied, a net current will be established, the sign being determined by the direction of the overvoltage relative to the equilibrium potential. At relatively low values of the overpotential or for charge transfer controlled reaction, the net current density is given by the Butler-Volmer equation below [6]

$$i = i_o \left\{ \exp[(1 - \beta)F\eta/RT] - \exp[-\beta F\eta/RT] \right\} \quad (6)$$

where η is the symmetry factor associated with the activation energy across the double layer. At large anodic overpotentials, i.e. at $\eta \gg RT/F$, the second term can be neglected while at large cathodic overpotentials, i.e. at $\eta \ll -RT/F$, the first term can be neglected. The equation can then be written in linear form to obtain the well-known Tafel equations. At even higher overpotentials however, the current density can not be sustained due to limitations on the transport of ions to and from the interface. The transport of ions to the electrode will not be able to keep up with the demand of electron flow. The overpotential of this concentration change is known as the concentration overpotential, η_c . For a purely diffusion limited or controlled process, the current density can be expressed as

$$i = i_L [1 - \exp(F\eta_c/RT)] \quad (7)$$

Although the preceding discussion dealt with a single electrode, it can readily be extended to a two-electrode system, e.g., an electroplating cell or corroding system, and the relevant equations would be similar in form. The equilibrium potential will be replaced by a mixed potential with a corresponding exchange current density. A combination of charge transfer and diffusion control is likely to be encountered for large current densities that are necessary to shorten the etching time of thick copper on the substrate. To overcome the effects of concentration polarization, some form of solution agitation would be necessary to ensure a constant supply of reactants to and transport of reaction products from the electrodes.

III. Experimental Procedure

A. Materials

The substrates used for the etching tests were PCB boards with 8.4 mil thick copper layers in place of the more expensive direct bond copper (DBC)-AlN substrates. This thickness is close to the 10-mil copper layer on most DBC-ceramic substrates.[7] A sprayable positive photoresist was used as the masking material to produce the test pattern on the substrates. For chemical etching, a commercial concentrated solution of ferric chloride (FeCl_3) was used while a standard copper plating solution was used for electrochemical etching.

B. Procedure

1. Imaging and patterning of substrate

The PCB substrates were cut into 2-inch x 2-inch squares and lightly polished with a 600-grit abrasive paper. The substrates were then ultrasonically cleaned with a degreasing detergent and alcohol. Finally, they were air-dried and baked on a hotplate to remove the remaining moisture. Several layers of photoresist were sprayed on each substrate until a relatively thick and smooth coating was obtained. A thick layer was found to be necessary for the mask to withstand prolonged etching times. The coated substrates were air-dried and subjected to a low-temperature bake at 80 to 85°C. The coated substrates were exposed in a flatbed ultraviolet (UV) exposure unit for a period of between 30 to 40 minutes. A prolonged exposure time was necessary because the photoresist coating was several times thicker than the normal thickness used. After exposure, the substrates were immersed in a developer solution to produce the desired pattern.

The test pattern consists of vertical and horizontal lines with nominal widths of 0.25, 0.5 and 1.0 mm. The total surface area is 2.00 cm². A schematic of the pattern is shown in Figure 1. The actual linewidths after exposure and development were wider than the nominal values as will be discussed later. Actual circuits were also patterned on the substrates to compare the quality and effectiveness of both chemical and electrochemical etching. All patterns were imaged using a black vinyl mask on transparent plastic. A precise mask with a small linewidth tolerance was not considered crucial to the experiment since the lines are relatively wide.

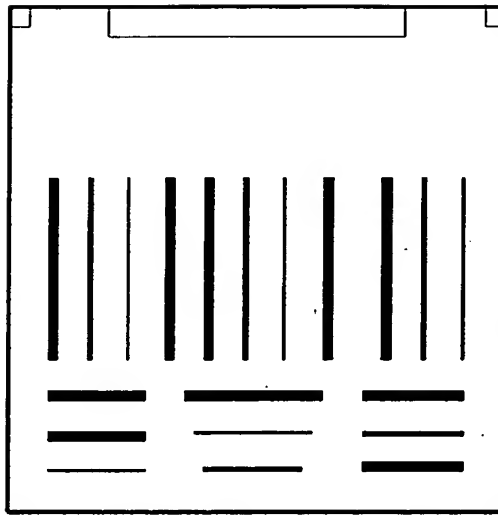


Figure 1. Test pattern for electrochemical etching tests on 2"x 2" substrates where dark areas are openings in the mask.

2. Etching of patterned substrate

Chemical etching of the test substrates was conducted in a heated 40% ferric chloride solution. Agitation of the bath was provided using a magnetic stirrer. Etching was carried out for about 2 hours or until the copper in the exposed surfaces was completely removed.

Electrochemical etching was carried out in a typical copper electroplating setup shown in Figure 2. It consisted of a flat copper plate or copper-coated PCB that served as the cathode and the test substrate which served as the anode. The two electrodes were mounted parallel to each other at a distance of about 3/8 to 1/2-inch. The surface area of the cathode was substantially larger than that of the exposed surface of the anode (test substrates) but this was not considered a primary concern since the removal of copper from the anode was more important. The entire fixture was then submerged in a copper plating bath. The bath had a composition[8] of 200 g/l $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 5 g/l H_2SO_4 , and 0.2 to 1.0 g/l Rochelle salt. A magnetic stirring bar was used to provide agitation to the plating solution. DC plating current was provided by a Tektronix power supply with a digital readout. The etching process remained in the constant current regime until the trenches became deep enough that it switched to the constant voltage regime close to the end of the process.

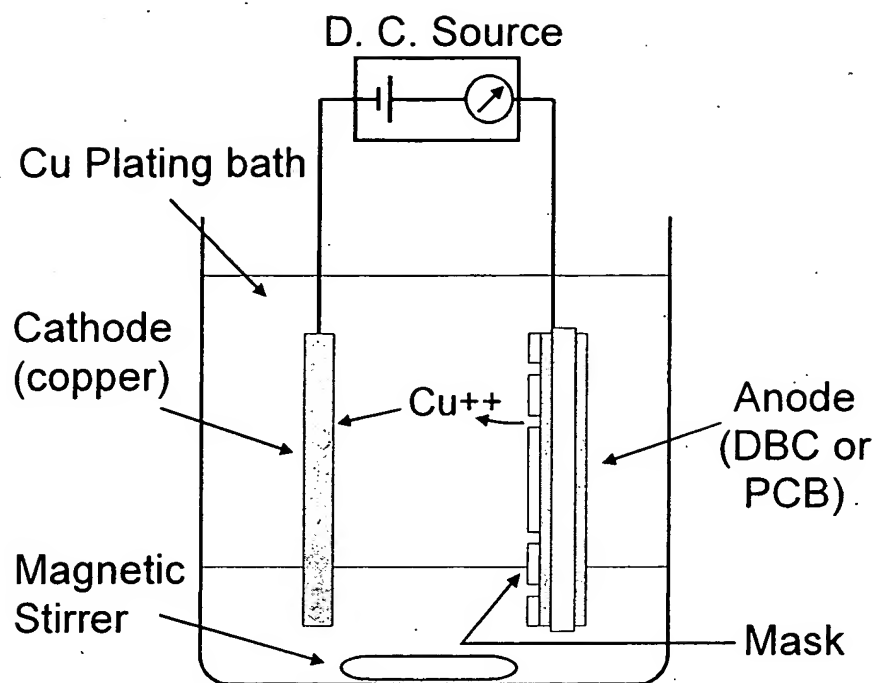


Figure 2. Schematic of the electroplating cell used for etching the copper on substrates.

The current densities used were 100, 150, 200 and 250 mA/cm. These current densities are higher than the range normally used for high-quality plating⁵ and required agitation to sustain the current density. The maximum voltage was limited to 3.0 V to prevent any potential side reactions from occurring when the process moves into the concentration polarization regime. This ensured that the chemistry of the bath was maintained close to the original composition and was reusable for subsequent runs. The etching process was also occasionally interrupted to wipe off oxidized copper that remained in the trenches and restore the current density to the desired level.

Minimum etching times for the current densities above were calculated using the following equation

$$t = \frac{WnF}{MI} \quad (8)$$

where M is the atomic weight of Cu, I is the total current, W is the weight of copper to be removed, F is the Faraday constant (96500 Coul/mol) and n is the valence of copper (equal to 2). The adjusted surface area of the test pattern was 2.25 cm² which was calculated from actual measurements of the dimensions of the lines. The calculated etching times are shown in Table 1.

Table 1. Calculated etching times for the current densities used. A 100 % efficiency is assumed in the calculations.

Current density (mA/cm ²)	Total current (mA)	Etching time (minutes)
100	225	92
150	338	61
200	450	46
250	563	37

The etching times were prolonged by a few minutes in each case to compensate for the inefficiency and non-uniform etch rate of the process. The endpoint was reached when a substantial drop in the current occurred and was not restored by increasing the voltage setting in the power supply.

After etching, each test substrate was sliced into several pieces along several planes and mounted in molding epoxy for observation under a microscope. The mounted samples were ground and polished down to 1 μm with alumina powder. The top and bottom widths, when applicable, were measured for each trench and the average value reported for each nominal width or gap.

The etching time for the circuit pattern was also calculated using Eq. 8. Larger currents were required since the open surface was 5.0 cm². A short final etch in ferric chloride was necessary to remove the thin isolated copper layers remaining in the trenches.

IV. Results and Discussion

The widths of the trenches etched on the copper were measured using an optical microscope compared with the initial or unetched line widths and the results from ferric chloride etching. Two sets of data were obtained, one for the surface and the other for the bottom of the trenches because it turned out that the etched width decreased with depth. These results are shown in Figure 3 and Figure 4, respectively, along with data obtained from substrates etched with FeCl₃. There is a widening trend in the width of the etched trench at the surface of the copper layer with increasing current density regardless of the original line width. An exception was at 250 mA/cm² but this was attributed to the thicker masks on the substrates that withstood the erosion from stirring and the shorter etching time. Within reasonable error, the amount of

widening at a given current density also appears to be insensitive to the original width of the exposed copper lines. The surface widths of trenches etched with FeCl_3 were comparable to those obtained by electrochemical etching at the higher current densities used. It should be noted that stirring of the FeCl_3 solution was also necessary to increase the etching rate but not necessarily as vigorous compared to the agitation of the electroplating bath. Figure 4 also shows an increase in the width of the bottom of the trench with increasing current density. However, they were not any wider than the original pattern except at the 250 mA/cm^2 current density. This can be attributed to the more vigorous agitation of the plating bath at increasingly higher current densities. The results also show that etching through the thickness of the copper at the lower current densities becomes more difficult as the gap or linewidth becomes narrower. This is caused by restricted fluid flow in the narrow trench that effectively lowers the etching rate. In fact the wider lines were observed to etch faster and deeper. This was partially eliminated by stronger agitation at higher current densities with the unwanted consequence of more widening and overetching of some of the lines.

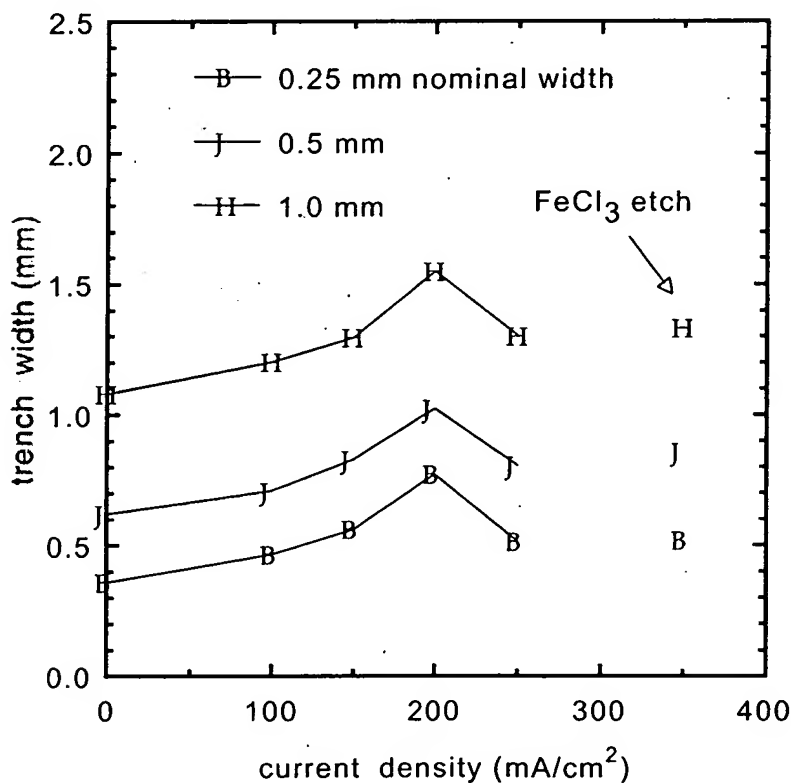


Figure 3. Plot of the surface trench width for various line widths, current density, and etching technique. Results from FeCl_3 etch are shown on the right as indicated.

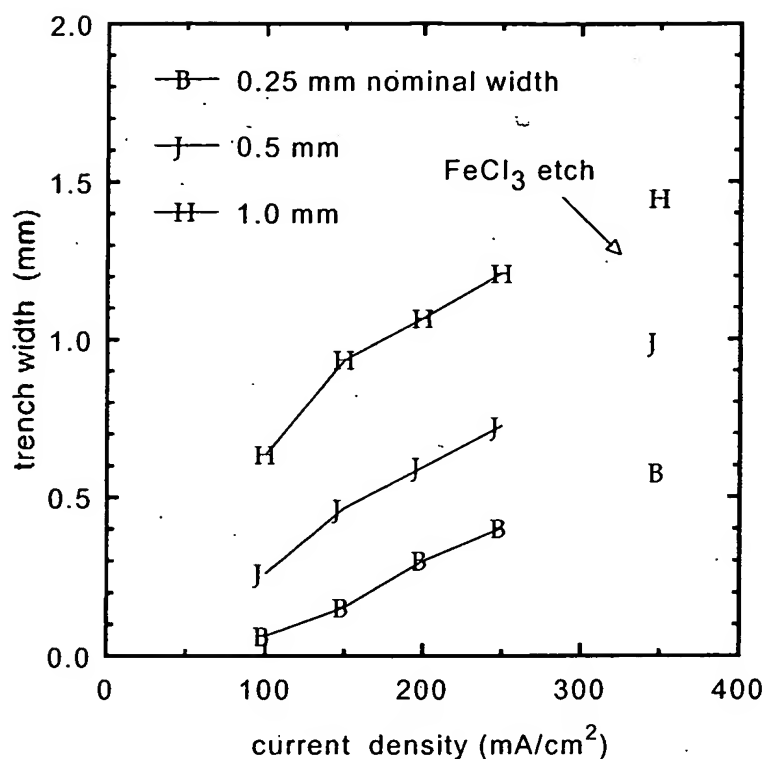


Figure 4. Plot of the bottom trench width for various line widths, current density, and etching technique.

The FeCl_3 etch actually resulted in wider bottom widths not only with respect to electrochemical etching but also relative to the width at the surface of the copper layer. This trend is not totally unexpected. Ideally, the etched trench should have a vertical wall on both sides as shown in Figure 5 (a). For the electrochemical method, etching rate is sensitive to the transport of reactants and products through the liquid boundary layer and the geometry of the exposed surface. The surface directly facing the cathode and the side walls closest to the cathode will etch faster than the surface hidden from view. Hence a rounded bottom will be etched as shown in Figure 5 (b). For an isotropic FeCl_3 etch that does not depend on an external potential, surface geometry is less of a factor such that undercutting will occur for sufficiently wide gaps as shown in Figure 5 (c). An actual trench obtained by electrochemical etch on copper is shown in Figure 6 (a) while Figure 6 (b) is that of a trench etched by FeCl_3 . For very narrow gaps with relatively poor agitation, widening at the bottom during FeCl_3 etching does not necessarily occur to the same extent as the wider gaps. Although widening has occurred in both cases due to the effect of agitation, the trench shapes are similar to those in Figure 5.

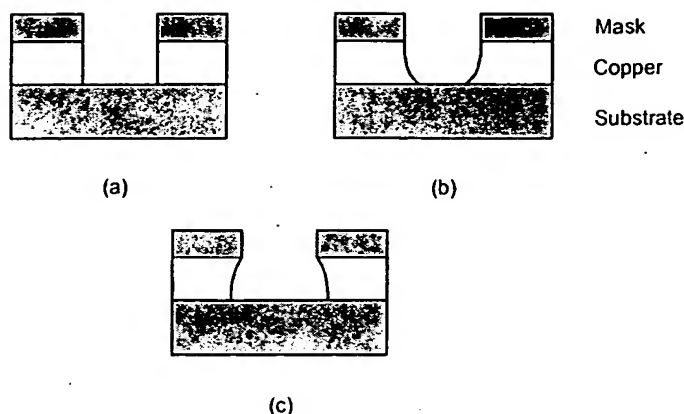


Figure 5. Schematic of the trench profiles for (a) ideal etch, (b) electrochemical etch, and (c) FeCl_3 etch without mask erosion.

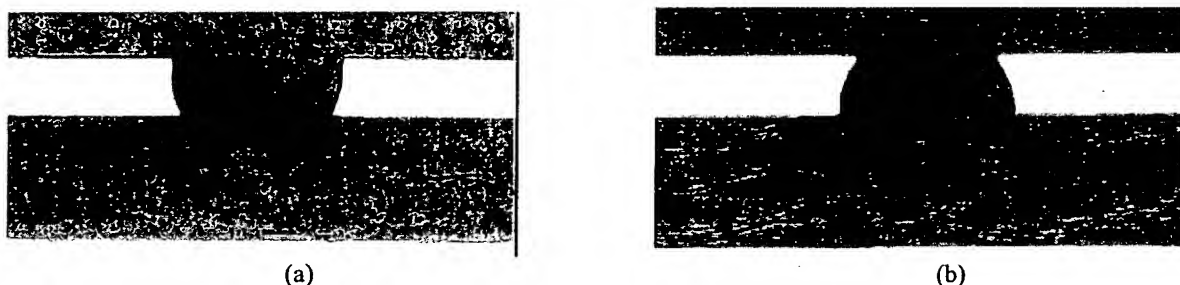


Figure 6. Cross-sectional images of trenches in the copper layer etched by (a) electrochemical method at a current density of 250 mA/cm^2 , and (b) ferric chloride solution. Initial mask opening is 0.25 mm .

Although it poses no problems for thin copper layers, undercutting of thick copper when etching with the FeCl_3 solution can put a limitation on the circuit line definition.[4] If the bottom of the gap is wider than the top, the line width has to be larger than twice the undercut on each side plus the widening due to erosion of the mask in order to prevent a break in the copper pattern. This problem can be aggravated when the gaps are very narrow which then requires a longer etching time. Consequently, the wider gaps suffer more overetching because of increased etching time for narrow gaps. With electrochemical etching, the issue that must be dealt with is the gap between copper lines that has to be etched. A very narrow gap will hinder the dissolution of the metal at the bottom because of slower diffusion of ionic species in solution and the limit on the throwing power of the plating solution.[9] This can be partly alleviated by a better agitation method and lowering the current density to more realistic levels.

The unwanted effects of solution agitation or stirring were asymmetrically etched trenches and non-uniform etch rates over the entire surface area. The wall surfaces facing the direction of

fluid flow experienced more dissolution than the opposite walls that are relatively shielded from the solution flow. This effect is more pronounced near the substrate periphery and the part close to the stirrer where the flow is more turbulent. The exposed surfaces at these locations also etched faster than the patterns in the middle. One potential solution to this issue is by using an ultrasonic bath to agitate or vibrate the plating solution.[10] Preliminary tests indicate that a relatively high current density can be sustained with this setup. Ultrasonic vibrations lead to the continuous displacement of the liquid relative to an equilibrium position and cause intense mixing of the plating solution. Cavitation voids also form and their subsequent implosion can produce localized shock, temperature increase and electrical discharge which in turn can lead to disintegration of the metal surface. Ultrasonic vibration can also influence electrode kinetics by affecting the polarization of the electrodes. Switching to a cheaper, more durable mask such as photodefinable solder mask. The solder mask can also be stripped easily by lightly sandblasting the mask off the substrate. We will continue to investigate and possibly adopt this method of masking and solution agitation for our future substrate requirements.

One other factor that contributes to the non-uniform etching is the variation in current density over the cathode and anode surfaces.[9] Calculations such as those done using Eq. 8 only provide average etching (or plating) rates. However, in practice, this is not achieved even for perfectly flat electrodes placed parallel to each other. The actual current density is higher at the corners and edges of the electrode. The distribution of the lines of force through which the current flows is sensitive to the location of the electrodes in the bath even though their relative positions and gap remain the same.

Finally, actual circuit patterns were etched with both methods to compare the quality of the etched circuits. The substrate shown in Figure 7(a) was electrochemically etched using a current density of 200 mA/cm^2 for 30 minutes and a current density of 100 mA/cm^2 for another 40 minutes. A short etch in FeCl_3 was done as a final step to remove the traces of copper still remaining. A second substrate shown in Figure 7(b) with an identical pattern was etched in heated and stirred FeCl_3 bath for about 2 hours. Overall, the resulting circuit patterns look very similar. Closer inspection however revealed sharper corners for the electrochemically etched copper circuits. The circuit lines were also wider at the bottom for reasons already discussed.

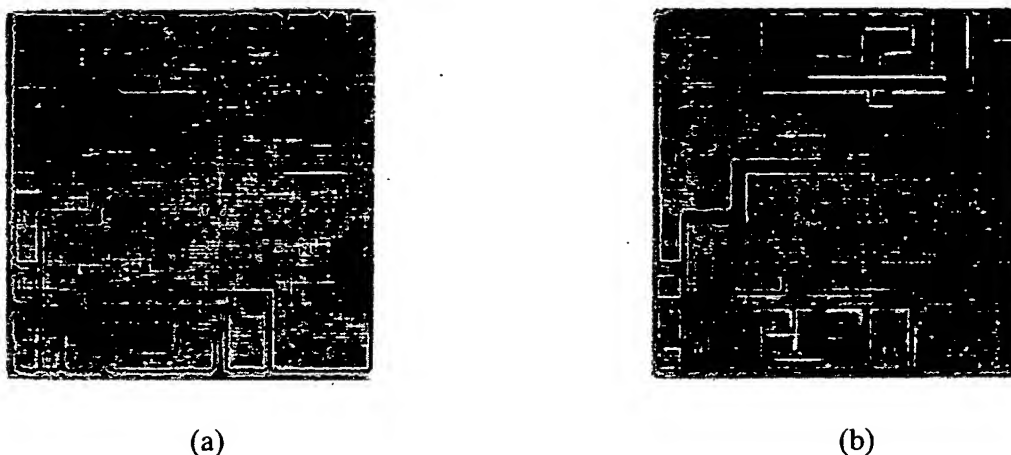


Figure 7. Circuit patterns on thick Cu PCB etched by (a) ferric chloride and (b) by electrochemical method followed by a short ferric chloride etch.

V. Summary

Copper circuit patterns were electrochemically etched on glass fiber-epoxy boards (FR-4) and direct bond copper (DBC) alumina boards with thick copper cladding. The results show that electrochemical etching is a viable alternative to ferric chloride etching. Etching times were shorter and the etched patterns were comparable if not better than those obtained by ferric chloride etch. Erosion of the mask due to vigorous solution agitation was observed in electrochemical etching but improved masking techniques and alternate agitation methods can minimize the problem. Nonuniform etch rates were also observed due to nonuniform agitation and current density. This can be minimized by switching to ultrasonic agitation and by improved plating cell design. Undercutting of the copper pattern was observed in ferric chloride etching but not in electrochemical etching. The bottom of the trenches were wider than the top for patterns etched in ferric chloride while the opposite is true for patterns that were electrochemically etched.

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